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Ford Motor Company
The American Road
Dearborn, Michigan 48121

July 23, 1990

Air Docket (LE-131)
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460

Attention: Docket No. A-90-16

The information provided with this communication reflects Ford Motor Company's comments on the June 5, 1990 Federal Register Notice regarding the May 9, 1990 Ethyl Corporation ("Ethyl") submittal of an application for a waiver of the prohibition on fuels and fuel additives set forth in Section 211(f) of the Clean Air Act, specifically for 1/32 gram/gallon (gm/gal) methylcyclopentadienyl manganese tricarbonyl (MMT). Comments regarding the aforementioned waiver application were requested to be submitted to EPA on or before July 22, 1990.

We have reviewed the results of Ethyl's most recent test program which was conducted in support of their subject waiver request. This program demonstrated the characteristic hydrocarbon increase which has been previously attributed to MMT. The results also exhibited an unexplained decrease in carbon monoxide and oxides of nitrogen emissions.

We have also examined the results of previous studies which have shown that, at higher concentrations (1/8 and 1/16 gm MMT/U.S. gal), MMT has a deleterious effect on vehicle emission control systems. In view of these incongruous findings, there is a particular need to demonstrate conclusively that similar effects will not be realized from MMT at the concentration proposed in the waiver request.

To approve the waiver, we believe that the following would have to be determined:

- that specific inspection and analysis of these components show the EGO sensors and catalysts on the tested vehicles were not adversely affected by the MMT;

- why the adverse effects that were clearly demonstrated at 1/8 and 1/16 gm MMT/U.S. gal gasoline are not so readily apparent in the 1/32 gm MMT/U.S. gal gasoline test fleet -- including an evaluation of the lack of additive packages in the test fuel; and

- that the 1/32 gm MMT/U.S. gal added to commercial grade gasoline containing standard additive packages (as opposed to the clear fuel used in Ethyl mileage accumulation) will not cause or contribute to the failure of a vehicle to comply with any applicable standard, including the standards that will take effect pursuant to imminent Clean Air Act amendments.

The attached text contains the in-depth discussion of these concerns and recommended test procedures.

Sincerely,

Kelly M Brown

D. R. Buist for

Attachments

cc: Ms. Mary T. Smith, Director
Field Operations and Support Division (EN-397F)
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460

# FORD MOTOR COMPANY'S COMMENTS IN RESPONSE TO ETHYL CORPORATION'S APPLICATION FOR WAIVER TO ALLOW METHYLCYCLOPENTADIENYL MANGANESE TRICARBONYL (MMT) AT 1/32 GRAM MMT/U.S. GALLON UNLEADED GASOLINE

Docket No. A-90-16

On May 9, 1990, Ethyl Corporation submitted a request for waiver to allow the use of MMT (marketed as HiTEC 3000) at the concentration of 1/32 gram (gm) MMT/U.S. gallon (gal) unleaded gasoline. Pursuant to this request, Ethyl has provided the results of an extensive test program which accumulated 75,000 miles on each of 48 vehicles, half of these being operated with the 1/32 gm MMT/gal added to the test fuel, to determine the effect of MMT on vehicle exhaust systems.

There has not been any information presented pertaining to chemical or physical analyses performed on the components of the emission system (i.e., catalyst, EGO sensor, fuel injectors, etc.). These tests could provide conclusive evidence regarding the effects of MMT on vehicle emission control systems. Further, although the test program provided some valuable information regarding the effects of MMT on exhaust emissions, it also raised several new concerns. We believe that these concerns need to be resolved, by the test procedures which are outlined below, before the waiver can be approved.

The following materials present our findings on analysis performed on catalysts from vehicles which were operated on fuel containing MMT (1/16 gm/gal), our concerns regarding the test protocol, and finally, our recommendations for the test procedures discussed above.

Ford Experience with MMT

Ford has just completed an analysis of 11 catalysts removed from Ford of Canada employee vehicles which have been operated on fuel permitted to contain MMT at a concentration of 1/16 gm MMT/U.S. gallon gasoline (refer to Attachment 1). The purpose of this investigation was to determine if the effects of MMT at a concentration of 1/16 gram MMT/U.S. gallon have a measurable effect on the emission control systems of vehicles which have not encountered a malfunction.

The results of this study indicate that the combustion product of MMT, $Mn_3O_4$, was the primary cause for the significant decreased efficiency of these catalysts (only trace amounts of other oxides of manganese were found on the catalysts). A 5 to 80-micron thick layer of $Mn_3O_4$ covered the washcoat and contributed to the mass transfer resistance, thus decreasing the efficiency of the catalyst for converting HC and to lesser degree, $NO_x$ and CO. The analytical data also showed that as mileage increased, the amount of manganese deposited on the catalyst washcoat also increased.

The above findings support those from previous analyses which were conducted on 41 catalysts from Canadian vehicles which were exposed to fuel permitted to contain 1/16 gm MMT/U.S. gal gasoline (refer to Attachments 2 & 3). These vehicles were returned for diagnostics because of poor driveability, and one or more malfunctioning components were discovered including the catalyst. Physical and chemical analyses of these catalysts have shown severe (5 to 30 microns) $Mn_3O_4$ buildup occurred on the catalyst washcoat. This $Mn_3O_4$ layer slowed the diffusion of the gas to the washcoat so that the conversion rates were reduced as mass transfer through the $Mn_3O_4$ layer became the rate controlling step. Over time, this layer would continue to thicken, further deteriorating catalyst efficiency. In severe cases, the $Mn_3O_4$ deposits blocked the cells of the catalyst, restricting the exhaust gas flow through the catalyst, creating increased back pressure, and in turn, poor driveability.

In conjunction with the 41-catalyst analysis, a catalyst was removed from a randomly-selected, well-maintained Ontario Provincial police car (5.8L 1978 LTD 58,120 miles, refer to Attachment 2). Analysis of this catalyst showed substantial inlet face plugging and significant catalyst efficiency deterioration for all three pollutants, HC, CO and $NO_x$. Although there were no apparent driveability performance problems observed for this vehicle, the contaminated catalyst exhibited nearly total loss in $NO_x$ conversion.

Although the problems we have experienced in our emission control systems, as described above, have occurred in cars exposed to levels of MMT twice that which are being proposed under the waiver request, it is clear that reduced MMT concentration will not eliminate combustion by-products, but will merely alter the rate of formation. Because the catalyst acts as a filtration system and removes most of the $Mn_3O_4$ which has not deposited on the combustion chamber or in the exhaust manifold, we believe the effects of MMT are proportional to its concentration in the fuel.

This proportionality was discussed in the SAE paper (790704), "Results of Coordinating Research Council MMT Field Test Program" (Attachment 4). The 63 vehicles tested in the field program used a fuel representative of a commercial gasoline for mileage accumulation (clear gasoline was used only for the emission tests). Comparisons of the vehicle emissions from the three sets of cars that comprised this fleet (containing 0 MMT, 1/16 gm MMT/gal and 1/32 gm MMT/gal) show that hydrocarbon conversion efficiencies decrease with increased MMT concentration. In addition, no evidence of decreases in CO or $NO_x$ emissions were observed in this test program.

Concerns Regarding Test Protocol:

Howell EEE fuel, used exclusively for exhaust and evaporative emission testing, was employed in the test program for mileage accumulation. However, under 40 CFR §86.113-90(a)(1), mileage accumulation fuels must be "representative of commercial gasoline which will be generally available through retail outlets". Such fuels, accordingly, contain deposit control additive packages to prevent deposit build-up in engines, injectors, and other components. Howell EEE does not contain these additives and is therefore not representative of commercially-available gasoline. Lack of fuel detergents would cause an increase in the combustion chamber or intake fuel system deposits and thereby result in an unrepresentative baseline as a reference point. Therefore, there is some reason to suspect the representativeness of Ethyl's data regarding the relative effects of MMT on in-use vehicles or to certification test vehicles. (Attachment 5, Figures 1-3)

We have compared the test program emission data for the Ford baseline vehicles to our own 50k durability data for cars of the same model and engine family. The cars operating on Howell EEE have substantially higher emission levels for both hydrocarbons and carbon monoxide. $NO_x$ emissions are also substantially different.

Another concern is that averaging the effects of MMT over the entire test fleet yields different conclusions than viewing individual vehicles. For example, although fleet average CO and $NO_x$ emissions are shown to be reduced through the use of MMT, four of the eight models tested have higher CO emissions and two of the eight have higher $NO_x$ emissions for the first 50,000 miles when operated with MMT. In fact, many of the significant gains in vehicle emissions are not realized until after high mileages have been accumulated. These transitions at high mileage often tend to coincide with completion of repairs, routine maintenance or, possibly, other systematic problems and should be analyzed further. (Attachment 5; Table 1, Figures 4-27)

Concern over Effects on Vehicle Emissions

It has been suggested that the data resulting from the MMT test program demonstrate that addition of MMT results in reduced $NO_x$ and CO emissions. Although hydrocarbon emissions were found to increase slightly (approximately 6% over 1,000 to 50,000 miles) it is claimed that this increase will not contribute to vehicle failure to meet the current HC emission standard of 0.41 gm/mile. However, there is no reason to believe that all vehicles will operate within the same compliance safety margin in customer hands. In addition, as mentioned above, although the 6% increase is the fleet average increase in HC emissions, some vehicle models exhibit substantially higher increases. Thus, the ability to meet proposed future HC standards may be sharply inhibited for the manufacturers of those vehicles.

There appears to be no definitive explanation for the $NO_x$ reduction. It has been suggested that it may be due to the catalytic behavior of the MMT combustion product, manganese oxide ($Mn_3O_4$), which admittedly coats the interior of the exhaust system. Although $Mn_3O_4$ does indeed have the ability to catalytically decompose $NO_x$, it is highly unlikely that this is the cause for the reduced emission levels. Catalytic decomposition of $NO_x$ by $Mn_3O_4$ is known to be too slow to be practical at the $NO_x$ levels found in automotive exhaust. Thus, no technical support is evident for the enhanced reductions in $NO_x$.

There are, however, many other possible explanations for the $NO_x$ reduction. These include:

- $Mn_3O_4$ deposits in the combustion chamber create "hot-spots" which affect the ignition point and serve to both decrease $NO_x$ and increase HC;

- oxygen sensors coated with $Mn_3O_4$ can change the engine air/fuel mixture from that intended by the engine design;

- $Mn_3O_4$ deposits on the fuel injectors may alter the spray patterns and/or prevent closure, thus increasing enrichment in one or more cylinders, leading to increased HC emissions, subsequently decreased $NO_x$, and possible imbalance in engine power generation;

- $Mn_3O_4$ deposits on the catalyst washcoat can lead to increased backpressure which will increase residual gas in the engine, thus increasing HC emissions and decreasing $NO_x$ emissions and possibly affect vehicle performance.

It is this uncertainty in the mechanism for $NO_x$ reduction which makes a greater in-depth analysis so critical in order to determine what is occurring within the vehicle emission control system. Some insight to this mechanism may be derived from the comparison of the constituents of the feed-gas to the tail-pipe emissions (Attachment 5, Table 2). Although very little engine-out data were provided in the waiver documents, from the few tables provided, the trend of increased HC and decreased $NO_x$, which is seen in the tailpipe and attributed to the activity in the catalyst, is present in the engine-out gas. This observation indicates that emission reductions for $NO_x$ and CO occur prior to the catalyst and are, therefore, unlikely to be the result of the catalytic characteristics of $Mn_3O_4$ but rather attributed to the mechanisms proposed above. SAE paper 790704, discussed above, further supports this conclusion.

The emission data from this extensive test program gave no evidence that MMT caused reductions in either CO or $NO_x$ emissions.

Moreover, we are concerned over the observed increase in hydrocarbon emissions. This percent increase is significant, particularly in light of the lower standards and doubling of the useful life compliance period proposed by Congress under pending Clean Air Act legislation that is expected to be enacted shortly. It has been stated that future emission requirements do not have to be considered as a matter of law in the EPA evaluation of this waiver request. Rather, compliance with existing standards need only to be considered. However, hydrocarbons are key ozone precursors, and it is the congressional concern for ozone problems which have prompted the legislative activity. Thus, it is inappropriate to ignore the legislative proposal that, starting with the 1993 model year, some of our cars will have to comply with a hydrocarbon standard of 0.25 gm/mile, a 39% reduction over current levels. Pending legislation also could reduce the hydrocarbon standard by an additional 50% by 2004 (0.125 gm/mile). It would be impractical to ignore the effects of MMT on emission levels in light of the reductions which are proposed for the near future before introducing this additive to vehicle fuels. In fact, the law is silent on the issue of future emissions standards. Therefore, EPA is clearly not precluded from considering this issue and in view of the virtual certainty of more stringent standards, we believe it would be inappropriate for EPA to grant a fuel waiver without considering its effect on the standards likely to be in effect when the waiver would be operative.

We would also like to emphasize that a waiver should be granted only if it is determined that the fuel or additive will not cause or contribute to the failure of vehicles to comply with any applicable emission standard. It is not sufficient basis to grant a waiver if EPA determines no such effect on $NO_x$ or CO emissions, but that the fuel or additive would cause or contribute to the failure to comply with HC standards.

Although improvements will be made in emission control systems in anticipation of these standards, MMT can be expected to aggravate the exhaust emissions in meeting the Tier I standards and compliance will be severely affected. In order to meet the proposed Tier I standards, the control system will have to maintain a tight air/fuel ratio (minimum amplitude and short duration of deviations in stoichiometry). This is possible only if both the emission and control systems are kept clean during the mandatory in-use compliance period. Any plugging of injectors or EGO sensors, or deposits on the catalyst, will cause a lean shift and slow response from the oxygen sensor and increase the diffusion barrier on the catalyst. Therefore, the emission control systems of the future will have an increased sensitivity to $Mn_3O_4$ deposits and any increase in engine-out emissions will have a larger percentage effect on tailpipe emissions.

In addition, promising advances in emission control technology has indicated emission benefits through the use of close-coupled catalysts. These catalysts, however, would be operating at higher temperatures, hence increasing their susceptibility to $Mn_3O_4$ deposits. Therefore, a hydrocarbon emissions could increase despite improved technology if MMT is included in vehicle fuel.

We are also concerned that we have seen no data regarding the effect of MMT on emissions of light-duty trucks. These vehicles comprise a fast-growing portion of the American vehicle fleet, and are also subject to pending reduced emission standards. Light trucks run "hotter" than passenger vehicles, which may lead to performance problems if MMT is added to the fuel. $Mn_3O_4$ is known to plate-out fast in hot environments so that buildups will develop faster in light trucks than in passenger vehicles.

Evaporative emissions also need to be considered. The effects of fuel composition on the evaporative emissions control system become more critical with the stringent test procedures recently proposed. An assessment of the effects of MMT on canister storage capacity and canister purge may be warranted.

Finally, we are concerned about the emissions of $Mn_3O_4$ which will result from the introduction of MMT in gasoline. Our analysis has indicated that approximately only 24% of the $Mn_3O_4$ formed by the combustion of MMT will be deposited on the catalyst. The remaining 76% is either deposited in the exhaust system or emitted into the environment. We have become increasingly aware of the composition of vehicle exhaust and the pending standards to control their release into the environment. Therefore, we are apprehensive regarding the addition of toxic $Mn_3O_4$ to our emissions at unknown levels.

<u>Recommendations for Further Evaluation</u>
We believe that a key factor in the determination of the effects of MMT is the post-mortem analyses of the components of the emission control system, in particular the catalyst and oxygen sensor from the test vehicles which have been operated on fuel containing MMT at the concentration of 1/32 gm MMT/U.S. gal gasoline. These analyses would include the following tests which should be performed on the catalytic converters and oxygen sensors after they have been removed and photographed:

- Analysis by x-ray fluorescence
- BET surface measurements
- Microprobe for contaminant depth profile
- Optical and scanning electron microscopic examination of the washcoat conditions
- Determination of catalytic converter efficiency by steady-state and light-off curves
- Determination of oxygen sensor efficiency by sensor response delay

Additionally, in order to determine the effects of MMT on actual, in-use vehicles, similar post-mortem tests should be conducted on catalytic converters removed at random from Canadian vehicles which have been exposed to MMT (similar to those used in Ethyl's test program). The analysis of catalytic converter attributes and performance (i.e., BET and efficiency) should sufficiently demonstrate the actual long-term effects of MMT on in-use catalytic converters. Although we realize that the concentration of MMT in the Canadian gasoline is twice that which is currently being proposed by Ethyl, we still believe that valuable information concerning the effects of MMT on emission control systems may be gathered from these tests.

The vehicles selected for these physical and chemical characterization tests should represent a statistically significant cross-section of all Canadian Provinces. The vehicles should have documented maintenance, driving, and fueling records. The analysis should be performed not only on the catalytic converters, but also on other emission components (i.e., oxygen sensors and fuel injectors) from each of the vehicles selected for testing.

Our final suggestion is to express our concern regarding the use of Howell EEE fuel for mileage accumulation in the baseline vehicles in their test program. As noted previously, this fuel, which lacks detergents, is not representative of commercially-available gasoline. To best discern the effects of MMT on vehicle emissions, the reference or baseline test cars should accumulate mileage on commercial gasoline and the second group tested with the same commercial fuel to which MMT was added.

Should this program actually be re-run with commercial-grade gasoline, we would further recommend that vehicles with the following be used to best simulate the emission control technology that will be available in the near future in compliance with proposed Tier I emission standards: mass air, dual EGOs, sequential electronic fuel injection (SEFI), and close-coupled catalysts. Although electrically heated catalysts are not yet ready for production, this technology may become necessary for compliance with proposed future stringent standards. Therefore, the effect of MMT on this catalyst technology should also be determined.

Furthermore, because the rate of $Mn_3O_4$ deposition is increased by high catalyst temperature, as well as laminar gas flow conditions prior to entering the catalyst, these features will have to be taken into account in the selection of the vehicles for the test fleet. Also, driving conditions which tend to raise catalyst temperature (i.e., engine loading) will have to be considered in order to determine the effects of MMT on in-use vehicles.

Recommendations to EPA

We do not believe that conclusive proof has been submitted to show that MMT will not cause or contribute to the failure of a vehicle to comply with the applicable standards. To the contrary, we believe that evidence exists that MMT combustion products will have a deleterious effect on the function of the emission control system. Therefore, we strongly recommend that EPA require additional testing and analysis of the effects of MMT on vehicle emission control systems before making their decision on this waiver request. To approve the waiver, we believe that the following would have to be demonstrated:

- that specific inspection and analysis of these components show the EGO sensors and catalysts on the tested vehicles were not adversely affected by the MMT;

- why the adverse effects that were clearly demonstrated at 1/8 and 1/16 gm MMT/U.S. gal gasoline are not so readily apparent in the 1/32 gm MMT/U.S. gal gasoline test fleet -- including an evaluation of the lack of additive packages in the test fuel; and

- that the 1/32 gm MMT/U.S. gal added to commercial grade gasoline containing standard additive packages (as opposed to the clear fuel used in Ethyl mileage accumulation) will not cause or contribute to the failure of a vehicle to comply with any applicable standard, including the standards that will take effect pursuant to imminent Clean Air Act amendments.

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# LIST OF ATTACHMENTS

Attachment 1: Ford report presenting results of recent analyses of 11 catalysts removed from Ford of Canada employee vehicles (operated on fuel containing 1/16 gm MMT/U.S. gal gasoline). These catalysts exhibit coating by $Mn_3O_4$ and resultant severe loss of conversion efficiency which is proportional to vehicle mileage.

Attachment 2: Ford report which details the results of analyses performed on 26 catalysts removed under warranty from Canadian vehicles. These catalysts were found to be coated, and to some extent plugged, by $Mn_3O_4$. Catalyst efficiencies were severely reduced. Attached to this report are the results of analyses performed on the catalyst of a randomly selected Ontario Provincial Police car.

Attachment 3: SAE paper, "Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT" (890582), presented by Ford Research. The report describes the findings of the analyses of 15 catalysts, also removed under warranty from Canadian vehicles. The findings were the same as those discussed above.

Attachment 4: SAE paper, "Results of Coordinating Research Council MMT Field Test Program" (790706), prepared by GM Research Laboratories, Exxon Company and Chevron Research Company. This study indicates that the use of MMT (at either 1/16 or 1/32 gm MMT/U.S. gal.) will increase HC emissions without effecting either CO or $NO_x$ emissions.

Attachment 5: Detailed analysis of Ethyl's test data to determine the effects of MMT on individual models. The following tables and figures are included in this attachment:

Table 1: Percent Effect of MMT over Baseline (Averaged over Range)

Table 2: Effect of MMT on Engine-Out and Tailpipe Emissions at 50k and 75k

Figures 1-3: Percent Difference - Ethyl Baseline versus Ford Certification Vehicle Emissions (HC, CO and $NO_x$)

Figures 4-30: Effect of MMT on Vehicle Emissions - Models C, D, E, F, G, H, I and T (HC, CO and $NO_x$)

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ATTACHMENT 1

FORD REPORT: ANALYSIS OF 11 CATALYSTS
FROM FORD OF CANADA EMPLOYEE VEHICLES